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WP1 SAMPO Task 2.2
- Sensitive analysing techniques

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Background

In a work package 2 (WP2), one of the objectives is to provide inputs for the ageing in polymeric components used in Nuclear power plants (NPPs). One of the suitable ways is to provide the techniques that can be used to measure thermal degradation in polymeric components component non-destructively. One key issue in developing the non-destructive monitoring techniques is to verify how the results obtained using non-destructively testing relates to the polymer condition and its ageing in real life conditions. Task 2.2 under WP2 is focussed at the development of a technique i.e. isothermal microcalorimetry (IMC), which can measure the thermal degradation non-destructively and closer to the temperature experienced by the material in NPPs.

Methods

A multichannel microcalorimeter (MC), which is commercially available and known as "Thermal activity monitor" (TAM III), designed by TA instruments, Stockholm was used. IMC is a versatile technique for studying thermal activity. It is one of the sensitive techniques in comparison to e.g. differential scanning calorimeters (DSC). Both type of instruments can measure a signal of the order of µW, however, the sample mass in IMC can be in grams (1-10 g) whereas, DSC uses milli gram sample mass. Therefore, the specific sensitivity in µW/g for IMC can roughly be at least 1000 times higher than for DSC [1]. This also means that endothermic or exothermic processes due to the chemical and /or biological and/or physical changes using TAM III, can be studied at 100 K lower than the DSC. For example, instead of accelerated thermal ageing at 150 °C, thermal degradation using TAM can be studied at 50 °C, which is much closer to the real-life operating temperatures.

Tests

IMC tests using a non-aged Ethylene propylene diene monomer (EPDM) rubber at three different temperatures 80 °C, 100 °C and 125 °C have been conducted. Microcalorimeter was operated in the isothermal mode during all the three different temperatures. The sample masses were 1.5 g, 1 g and 0.5 g while calorimeter was maintained at 80 °C, 100 °C and 125 °C. The samples were placed in the airtight steel ampoules. IMC measurements were performed as per the standard test procedure recommended by the manufacturer. Steel ampoules along with the samples were held in the calorimeter for 15 min so that steel ampoules and sample will be in thermal equilibrium with the calorimeter. After 15 min of preheating ampoules were placed onto the calorimeter. Even the steel ampoules along with the samples were preheated as aforesaid, still the slight difference between the temperature of the ampoules and calorimeters can produce results with higher uncertainty. Therefore, 45 min of the data from the start of the experiments (after 15 min) was not considered for the heat calculations.

Results and discussion

As shown in the Figure 1, the measurable heat flow from EPDM can be seen at all three different temperatures. In comparison to the heat flow at 125 °C and 100 °C, the heat flow at 80 °C is significantly lower. The baseline stability of the TAM III was between 0.1 - 0.2 µW, therefore, the heat obtained from EPDM rubber at 80 °C can be considered due to thermal

degradation of the sample. For better clarity the heat flow at 80 °C in µW/g on Y-axis can be seen Figure 2.

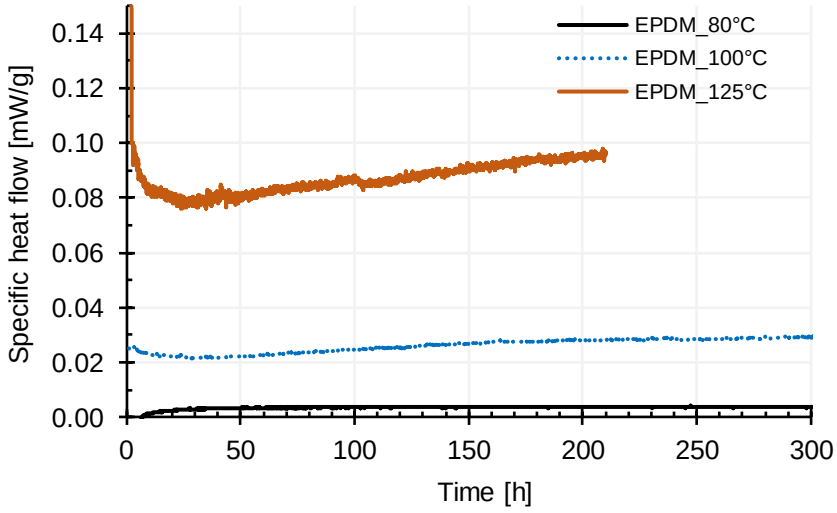

Figure 1. Specific heat flow (mW/g) for EPDM rubber sample at 80 °C, 100 °C and 125 °C.

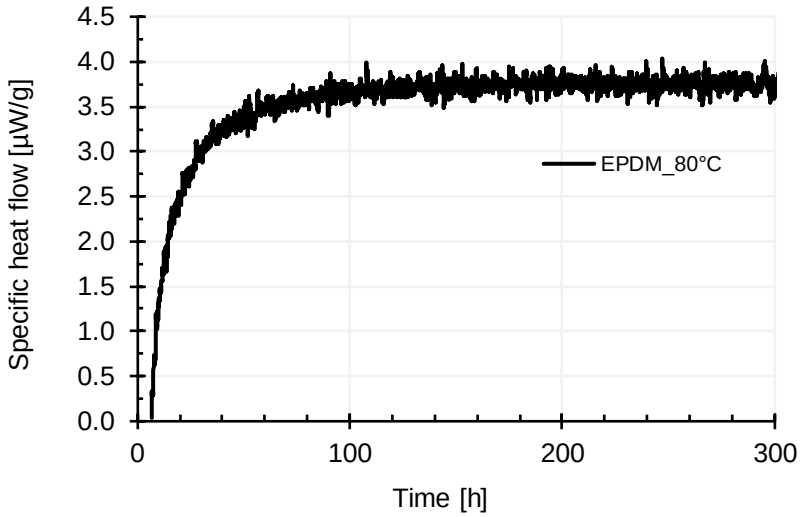

Figure 2. Specific heat flow (µW/g) from EPDM rubber at 80 °C.

Figure 3, shows the specific integrated heat at three different temperatures obtained by integrating the area under the specific heat flow curves (c.f. Figure 1). The heat flow measurements at 80 °C took about 2 weeks, 100 °C about 3 days and 125 °C about 24 h.

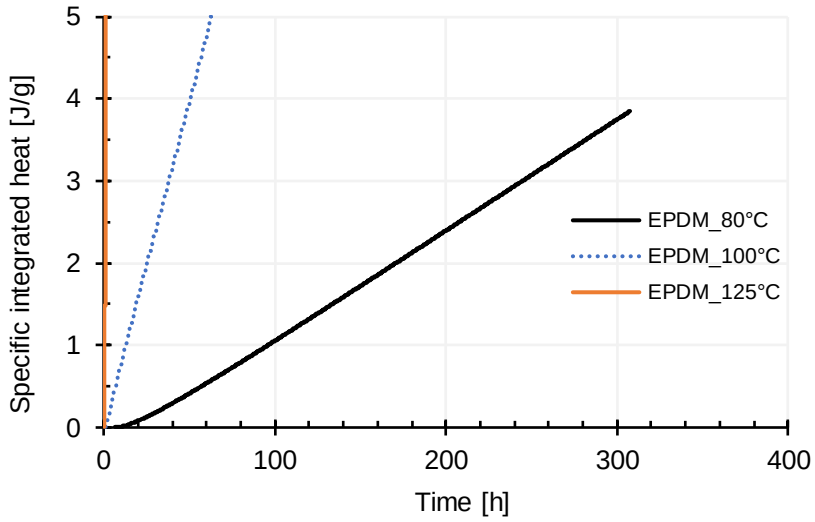

Figure 3. Specific integrated heat (J/g) for EPDM rubber at 80 °C, 100 °C and 125 °C.

Calculation of Activation energy

The temperature dependence of a reaction rate (*k*) can be studied assuming it follows an Arrhenius equation (1). Multiplying heat of the reaction (Q J/g) on both sides of the equation 1 and by taking natural logarithm represents an equation of a straight line *c.f.* equation 2. The activation energy Ea (kJ/mol) and combined term $Q \times A$ (J/kg.s) can be calculated from plotting ln $\dot{q}$ (specific heat flow) as a function of $1/T$ (Temperature in K), *c.f.* equation 2. Activation energy, *Ea* (kJ/mol), is obtained from the slope of the linear fit, which is equal to $-E/R$. The combined term $Q \times A$ (J/kg.s) is obtained by taking the exponential of the intercept on the Y-axis at time zero (see 2). As the heat flows were changing during the measurements, *i.e.*, the reaction rate was influenced by the extent of the reaction during the experiment. Therefore, the activation energy is calculated using specific heat flow measured at the same extent of reaction, at the different temperatures. The extent of reaction is proportional to the heat of the reaction (J/g), so the Arrhenius plot was made with specific heat flow assessed at the same amount of produced heat (J/g). An example of ln $\dot{q}$ versus $1000/T$ with a linear fit is shown in the Figure 4.

$$k = Ae^{\frac{-E}{RT}} \qquad (1)$$

$$ln(\dot{q}) = ln(Q \times A) - \frac{E}{RT} \qquad (2)$$

R = Universal gas constant 8.314 J.mol^{-1}.K^{-1}
Q = heat of reaction, J.kg^{-1}
A = rate constant, s^{-1}

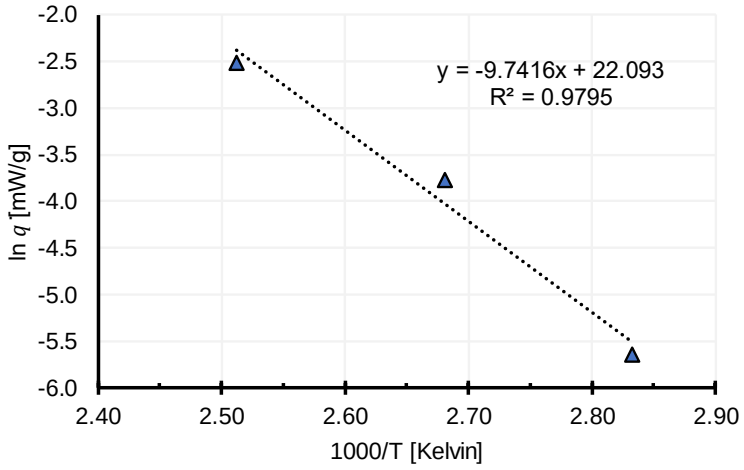

Figure 4. Linear fit for ln q dot (mW/g) versus 1000/T (kelvin) used for evaluation of activation energy.

The activation energy obtained by aforesaid procedure is shown in the Figure 5.

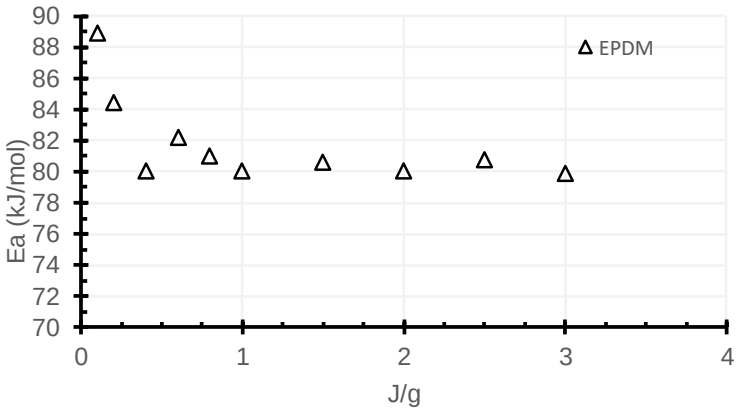

Figure 5. Calculated values of the activation energy (kJ/mol) for different extent of reaction (J/g).

The value of activation energy 110 kJ/mol, for highly filled EPDM rubber used in nuclear power plant is obtained by measuring the change in mechanical properties that is Young's modulus, indentation modulus and strain-at-break [2]. The changes in the mechanical properties were measured by thermal treatment of the EPDM between 110 °C and 170 °C. The thermal treatment at higher temperature most likely responsible for the hardening of the rubber and therefore, induce diffusion limited oxidation.

Future work

The value of the activation energy for EPDM rubber used in nuclear power plants needs further investigation. IMC measurements will be carried out at different temperatures for example 60 °C, 70 °C and 90 °C using same EPDM sample as presented in this report and other polymeric materials. Similar tests will also be carried out using pure polyethylene and polyamide 6, which will be helpful to compare the activation energy obtained at different temperatures for the pure materials.

References

[1] Wadsö L. Measuring chemical heat production rates of biofuels by isothermal calorimetry for hazardous evaluation modelling. Fire and Materials 2007;31(4):241-55.

[2] Pourmand P, Hedenqvist MS, Furó I, Gedde UW. Deterioration of highly filled EPDM rubber by thermal ageing in air: Kinetics and non-destructive monitoring. Polymer Testing 2017;64:267-76.